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(54) Catalyst and method for producing the catalyst.

(57) This invention relates to a catalyst and a method for producing said catalyst. At least 60 per cent by weight of the catalyst consists of copper oxide, aluminium oxide -spinel and 60-100 per cent of the copper present is bound to aluminium oxide as copper oxide, aluminium oxide -spinel where the atomic ratio Cu:Al = 9.25-0.50. The catalyst itself contains 1-20 per cent by weight of zinc oxide which is present in the pores of the spinel. Further amounts of zinc oxide may be admixed mechanically or be present as a coating on the catalyst. The catalyst is expecially well suited for conversion of carbon monoxide with steam. The catalyst is produced by precipitation of copper- and aluminium salts at pH = 6.0 - 6.5 during addition of an ammonium or alkali carbonate solution. After filtration and drying, the products is calcined at 750 - 850°C until it is obtained 60-100 per cent spinel structure. Zinc salt is instroduced in the pores of the spinel, and the product thereby formed is heated up to at least the decomposing temperature for the zink salt which is then converted to zinc oxide. Possible addition of zinc oxide in addition so that introduced to the pores of the spinel may be admixed mechanically.

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Croydon Printing Company Ltd.

Catalyst and Method for producing the Catalyst

The present invention relates to a catalyst containing aluminium oxide and copper oxide. At least 60 per cent by weight of this oxide mixture consists of a copper oxide, aluminium oxide compound with a spinel structure.

The invention also comprises a method for preparing the catalyst. Such catalysts are prepared by precipitation of metal salts, filtering, drying, calcining and forming to pallets or the like.

Catalysts as described above are well suited for the conversion of carbon monoxide with steam to form hydrogen.

The conversion of carbon monoxide with steam is a well known process. By means of suitable catalysts, the reaction, usually called the CO-shift reaction, can be carried out a temperature of about 200° C according to the equation:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

A number of catalysts for this purpose are described in the literature. Such catalysts usually contain copper distributed in an oxide matrix. This matrix may consist of Al_2O_3, Cr_2O_3, ZnO and MnO, or a mixture of two or more of

these components. The copper content is usually in the range of 20-40 per cent by weight, and most of these catalysts make it possible to carry out the reaction at 200-230° C.

A catalyst of this type is described in British patent No. 1,131,631.

It has been considered important to obtain the highest possible dispersion of the copper phase because this will lead to a large copper surface, and the tendency for sintering is reduced. According to the patent mentioned above, a good dispersion of copper is obtained by precipitating a slightly soluble product from a solution of copper-, aluminium- and zinc nitrates with a solution of sodium carbonate. The precipitated product consists of aluminium oxide and a mixed hydroxycarbonate of copper and zinc. The composition of this hydroxycarbonate depends on the conditions during precipitation. By heating to about 300° C one obtains a product in which copper- and zinc oxide are present in a very intimate mixture. Because these two oxides have a low solubility in each other, they exist accordingly as separate phases. By reduction of this oxide mixture with hydrogen one obtains the active catalyst for the CO-shift reaction.

A number of patents, among others US-patents 3,303,001 and 3,388,972, describe preparation of catalysts by coprecitation of copper-, zinc- and aluminium compounds. A catalyst with high initial activity is obtained from coprecipitation of aluminium hydroxide and copper hydroxycarbonate, and decomposition of the precipitate after drying at a temperature of 300-400° C. However, this catalyst has been found to be less stable than the above described catalysts containing zinc oxide.

A catalyst of a somewhat different type is described in US-patent No. 3,787,332. This catalyst consists mainly of an oxide mixture of copper and at least one of the trivalent metals aluminium, manganese, iron and cobolt. At least 60 per cent by weight of the oxide mixture shall have a spinel structure. The catalyst may also contain bivalent metals as magnesium, cobolt and cadmium. This catalyst is prepared by mixing a solution of a copper salt and a solution of at least one of the trivalent metals.

A gel-forming compound is added, and the gel is heated to at least 200° C for decomposing the gel and forming the spinel. When preparing the copper oxide, aluminium oxide catalyst, the gel is heated to 650°C for two hours. The catalyst is stated to have a high activity, and to be more stable than a catalyst with comparable composion, but without a spinel structure.

The disadvantage of this catalyst is that it is not resistant against chlorine- and sulphur contaminants and therefore requires a very clean gas mixture.

The zinc oxide containing catalysts referred to above are considerably more resistant to chlorine and sulphur fouling than the above described copper oxide, aluminium oxide spinel catalyst. The lifetime by technical usage of these zinc containing catalysts is therefore longer than for the spinel catalyst, which on the other hand, can more easily be given a higher mechanical strenght and it is not weakend as much during application.

One object of the present invention was to develop a catalyst having an activity at least as high as the previously known catalysts and retaining the activity

for a longer time.

Another object was to prepare a catalyst which in addition to high activity and stability also was resistant against poisoning, particularly against chlorine in the process gas.

Still another object was to prepare a catalyst where the active component has the highest possible dispersion in the catalyst.

Furhter it was an object to prepare a catalyst with improved mechanical properties.

For catalysts of the type described above for the CO-shift reaction, it has often been assumed that the active phase is metallic copper, and that the metal oxide phase only serves to separate the copper crystallites. The metals in the oxide phase are chosen in view of that assumption, and in order to obtain a compound between copper and the other metals in the precipitate. Thus by precipitating copper and zinc from their nitrates with sodium carbonate a slightly soluble copper, zinc-hydroxy-carbonate is formed with a structure similar to malachite.

By precipitating a mixture of copper and aluminium compounds from their nitrate solutions with a ammonium- or sodium carbonate solution, two compounds are formed. One is an aluminium oxide with a water content depending on the conditions during precipitation. The other product is a copper-hydroxy-carbonate with a structure similar to malachite. By suitable conditions during precipitation, these compounds can be made x-ray amorphous.

It is possible from this product to obtain a very active catalyst, but it is difficult to achieve the same stability as with a well formulatet ZnO/Cu or $ZnO/Al_2O_3/Cu$ catalyst (for example those described in British patent No. 1,131,631).

In order to increase the stability of a catalyst based on copper oxide and aluminium oxide the inventor tried heating to 650° C of the above mentioned precipitate of copper and aluminium as recommended in US-patent No. 3,787,332. However, this did not give the product the expected increase in activity and stability. Furthermore, the product had an unexpected low content of spinel.

Surprisingly, the inventor found that an unusually stable and active catalyst could be made by heating the above mentioned x-ray amorphous product to a higher temperature than that taught by US-patent No. 3,787,332. It also appeared that pellets made from this product could be given better mechanical properties than pellets from products as those described in British patent No. 1,131,631 and US-patent No. 3,388,972.

Though it was possible in this way to obtain an active and stable catalyst, it did not have the required resistance against poisoning from chlorine and sulphur. It is well known that zinc oxide has a positive effect against such poisonings. But introducing zinc oxide by coprecipitating zinc-, copper- and aluminium salts before calcination will prevent formation of the copper oxide, aluminium oxide spinel. In fact, if zinc oxide is present during the calcination stage, then a zinc aluminium oxide spinel will then primarily be formed and sintering of the copper oxide phase will simultaneously take place.

The inventor then tried to add zinc oxide to the copper oxide, aluminium oxide spinel. By addition of a zinc salt in a special way, a surprisingly high effect of the incorporated zinc oxide was obtained. The spinel was namely first impregnated with an aqueous zinc salt solution and then heated to a temperature high enough to decompose the zinc salt to zinc oxide, giving a uniform distribution of the zinc oxide in the pores of the spinel.

A special advantageous way of carrying out the impregnation was to precipitate partly or completely the impregnated zinc salt by an aqueous ammonium or alkali carbonate solution.

For further protection of the catalyst against poisoning, it may be convenient to mix it mechanically with zinc oxide powder or to coat the pellets with zinc oxide. In some cases it has been found that it may be practical to add up to 15 per cent by weight of zinc oxide in this way.

The special features of the catalyst according to the invention and the new method for preparing the catalyst, are defined in the present claims.

The preparation and the advantages of this catalyst will be explained in more detail and demonstrated in the following examples and tables. The first two examples relate to the preparation of a dried precipitate, which is converted to a copper oxide, aluminium oxide spinel by thermal treatment as described in Example 2 and 6.

The Examples 3-5 and Example 7 describe impregnation of products from Example 2 and 6 respectively. The products thereby formed give catalysts according to the invention.

Example 8 describes preparation of a known catalyst and this example is used for comparison.

Example 1

This example shows the preparation of a dried copper, aluminium salt which is the starting material for the preparation of a copper oxide aluminium oxide spinel. An aqueous solution of copper- and aluminium nitrate was made by dissolving

60,4 g /$Cu(NO_3)_2 \cdot 3H_2O$ and 187,5 g $Al(NO_3)_3 \cdot 9H_2O$ per litre solution, such that the concentration of Cu and Al became 0.25 and 0.5 molar respectively. Another aqueous solution was made by dissolving 288 g $(NH_4)_2CO_3$ per litre solution. These two aqueous solutions were pumped to a vessel at such a relative rate that the pH in this vessel was maintained at 6.0-6.5.

The two solutions were introduced under constant stirring in the vessel, and the temperature was maintained at 20° C. By maintaining these conditions a light blue precipitate was formed, which was filtered off and washed with water to make the NH_4NO_3 content in the dried product less than 5 per cent by weight. The product was then dried at 80-90° C till the remaining content of moisture got below 25 per cent and then the product was crushed to a particle size less than 0.5 mm.

Example 1b

This example does also show preparation of a dried copper, aluminium salt as starting material for preparation of a spinel. The preparation was carried out as in Example 1, but instead of a ammonium carbonate solution it was now

used an alkali carbonate solution containing 324 g Na_2CO_3 per litre solution. A light blue precipitate was also formed in this case and it was separated by filtration-and washed with water. The precipitate was washed till it contained less the 0.1 per cent by weight of Na, calculated on the dried product. This product was then dried and crushed in the same way as in Example 1.

Example 2

The product from Example 1 was heated in air to a temperature of 550° C for one hour, and then cooled to room temperature. Then 3 per cent by weight of graphite was added and the product was shaped in a tabletting press to cylindrical tablets with diameter and height of 5 mm. The cylindrical tablets were then calcined at 825° C for 30 minutes. This thermal treatment lead to the formation of the $Al(Cu, Al)O_4$-spinel as detected by x-ray diffraction. 75 per cent of the copper was bound to the aluminium oxide in the spinel, which had a atomic ratio Cu:Al = 0.35. The total content of copper was 28 per cent by weight. This product is designated as product A.

Example 3

Products A from Example 2 was impregnated with $Zn(NO_3)_2$ by dipping in an aqueous 3 molar $Zn(NO_3)_2$-solution. Subsequent to the impregnation the product was heatet to 350° C, whereby the zinc nitrate decomposed to ZnO. The impregnated product had a content of ZnO of 11 per cent by weight of Zn. This product is designated product B.

Example 4

Product A from Example 2 was first impregnated by zinc nitrate in the same way as in Example 3. The impregnated product was then di-ped in a 1 molar NH_4HCO_3-solution and kept there for about 5 minutes. Subsequent to this treatment the product was heated to 350° C for formation of zinc oxide. This product had a content of ZnO of 8 per cent by weight, i.e. 6.5 per cent by weight Zn, and 75 % of the copper was bound to the aluminium oxide in the spinel. This product is designated product C.

Example 4b

The product from 1b was further treated as stated in Example 2. The product formed and product A were both impregnated by aqueous solutions which both contained 16 g per litre ZnO and 288 g per litre $(NH_4)_2CO_3$. Subsequent to this treatment the two products were heated to 350° C for formation of zinc oxide.

The products contained 2,5 per cent by weight ZnO, i.e. 2 per cent by weight Zn. 75 per cent of the copper was bound to the aluminium oxide in the spinel. Both these products are designated Products C' because they proved to have the same properties as product C regarding catalytic activity, stability and resistance to chlorine poisoning.

Accordingly, application of alkali carbonate instead of ammonium carbonate resulted in a final catalyst having equally high quality. To obtain this quality it is important to wash most of the alkali salt out of the precipitate.

Example 5

Product A was impregnated by dipping in melted $Zn(NO_3)_2 \cdot 6H_2O$ at 60° C and was then heated to 350° C for formation of zinc oxide. This product had a content of ZnO of 4 per cent by weight and is designated product G.

Example 6

A sample of the product from Example 1 was heated directly to 825° C without subsequent tabletting and kept at this temperature for 60 minutes. After this heating step the products was formed to tablets of the same size as in Example 2.

95 % of the copper was bound to aluminium oxide in the spinel which had a atomic ratio Cu:Al = 0.37. The total content of copper was 37 per cent by weight. This product is designated product D.

Example 7

Product D was impregnated and heated to 350° C in the same way as described in Example 4, whereby a product was formed containing 8 per cent by weight of ZnO. The atomic ratio Cu:Al and the percentage of copper bound in the spinel was the same as in Example 6. This product is designated product E.

Example 8

This example shows the preparation of a conventional CO-shift catalyst prepared by co-precipitation of zinc-, copper- and aluminium salts.

An aqueous solution of copper-, zinc- and aluminium nitrate

was prepared by dissolving 40.3 g $Cu(NO_3)_2 \cdot 3 H_2O$, 59,8 g $Zn(NO_3)_2 \cdot 6H_2O$ og 62,5 g $Al(NO_3)_3 \cdot 9H_2O$ to a volume of 1 liter.

An other aqueous solution was prepared by dissolving 96 g of $(NH_4)_2CO_3$ to a volume of 1 liter. These two solutions were pumped to a vessel in such relative amounts that the pH in the vessel became 6.0-6.5.

The two solutions were supplied during constant stirring in the vessel where the temperature was kept at 20° C. When the above stated conditions were observed, a light blue precipitation was formed and it was separated by filtration and washed with water till the content of NH_4NO_3 in the dry product was below 5 per cent by weight. The product was then dried at 80-90° C till the remaining moisture was below 25 per cent by weight and it was then crushed to particles less than 0.5 mm.

After having been crushed, the particles were heated to 350° C and kept at this temperature for one hour. The particles were tabletted in the same way as in Example 2. The resulting tablets are designated <u>product F</u>.

The products B - F were used as catalysts during conversion of carbon monoxide with steam.

Before the conversion itself, the catalyst was reduced according to known procedure by heating in a hydrogen atmosphere having a hydrogen pressure of about 200 kPa. The temperature was increased by 30° C per hour until the temperature reached 250° C and this temperature was maintained for 3 hours.

The conditions during the conversion are listed in the respective tables.

The catalyst activity was measured in two different scales. For the results referred to in tables I and II it were used 1 litre of catalyst placed in a tubular reactor having an inner diameter of 38 mm. The CO-containing gas was drawn from a technical ammonia plant and the gas was drawn from a point positioned after the high temperature shift converter. This gas contained trace amounts of chlorine.

For the results referred to in tables III and IV it were used a tubular reactor having an inner diameter of 5.5 mm. This reactor was filled with 50 cylindrical catalyst tablets having a diameter of 5 mm and a hight of 5 mm, and between each tablet there was places a 5 mm glas sphere.

A highly prified gas, consisting of 95 % nitrogen and 5 % carbon monoxide, and water vapour (steam) were passed through this catalyst layer. Water was added in liquid form and vapourized under pressure. Hydrogen chloride was added to the water to a concentration of 0.005 mol HCl/litre such that the process gas thereby contained about 1.5-1.6 ppm HCl during the test.

The water present in the gas was removed before the gas was analyzed at the inlet and outlet of the reactor. The percentage carbon monoxide converted was calculated according to the following equation:

$$\%\ \text{reacted CO} = \frac{\text{vol. \% CO at the inlet} - \text{vol. \% CO at the outlet}}{\text{vol. \% CO at the inlet}} \cdot 100$$

In the table the degree of conversion with respect to CO is given for the different products (B-F) as function of period of operation in hours.

Table I - Activity Test

Catalyst	% CO conversion				
	0 hours	120 hours	240 hours	360 hours	480 hours
D	85	72	60	50	40
F	85	72	66	55	54

Test conditions:

Pressure: 24 bar, Temperature: 215° C, Space velocity: 1266 h^{-1}
Gas composition at the reactor inlet: (vol. %):
CO: 1,0-1,2 %, CO_2:16-17 %, H_2O: 41-44 %, N_2:17-18 %, H_2:51-53 %.

Table II - Activity Test

Catalyst	% CO conversion					
	0 hours	120 hours	240 hours	480 hours	720 hours	960 hours
C	82	82	82	82	82	82
F	74	65	62	62	62	62

Test conditions:

Pressure: 15 bar, Temperature 217° C, Space, Space velocity: 2026 h^{-1}
Gas composition at the reactor inlet (vol. %):
CO: 1,5 - 1,6, CO_2:12-13, H_2O:30-35, N_2:13-14, H_2:41-42.

Table III - Activity Test

Catalyst		% CO conversion						
Type	Amount in grams	0hours	10hours	20hours	30hours	40hours	50hours	3hours *
A	4,37	98	97	95	87	60	43	87
C	4,79	98	98	98	96	93	92	93
D	4,17	98	95	93	80	50	20	86
E	4,47	98	98	96	96	92	88	90
F	6,55	90	82	80	78	63	61	60

Test conditions:
Pressure: 10 bar, Temperature 180° C, Gas load: 1500 Ncm^3/min
Gas composition at the reactor inlet (vol. %):
CO: 2,85 %, N_2:54,28 %, H_2O:42,85 %, HCl:1,5-1,6 ppm

*Gas load: 3000 Ncm^3/ min

Content of zinc in per cent by weight of the catalysts C, E and F were 1,6 %, 1,2 % and 22,10 % respectively.

Calculated on basis of the contents of copper oxide-aluminium oxide 93 % are converted to spinel structure for the catalysts A and C and correspondingly for the catalysts D and E are 98.5 %.

Table IV - Activity Test

Catalyst		% CO conversion			
Type	Amount in grams	0 hours	10 hours	30 hours	60 hours
C	4,71	96	95	94	94
B	5,24	84	82	75	75
G	5,50	86	75	62	58

Test conditions:

The same conditions as for table III.

The contents of zinc as Zn in the catalysts C, B and G were respectively 6,5 9,1 and 3,2 per cent by weight.

Table V - Mechanical Properties

Properties	Catalyst			
	D	D*	F	F*
Tablet height (mm)	4,0	4,0	4,6	4,4
Tablet diam. (mm)	5,1	5,1	5,1	4,9
Tablet density (g/cm^3)	1,83	1,82	1,48	1,44
Breaking strength **	4,0	2,0	7,4	0,2
Change in weight (%)		-2		-19
Change in volume (%)		-0,4		-10

* Measured after the catalyst was removed from the reactor.

** Load (kp) against the cylinder wall of the tablets necessary for crushing them.

Change in volume is due to shrinkage of the tablets. The linear shrinkage was about 4 % for F which gives a volometric shrinkage of 10-12 % or -10 as stated in the table.

Table I and III show that catalysts of type A and D are not stable when the process gas contains chlorine. The chlorine content of the gas used for the tests described in table I and II are not known. The amount HCl present in the water supplied in the test shown in table III gives a chlorine content in the process gas of about 1.6 ppm. This is substantially higher than what is the case for table I and II.

Table II and III show that a substantially more stable catalyst (product C and E) are obtained when zinc oxide is added to the copper oxide, aluminium oxide -spinel catalyst. The initial activity is also higher for such a catalyst than for a catalyst without zinc oxide. This was proved by doubling the gas load for the test shown in table III, and this increase in gas load was done about 3 hours after the test started. The results are shown in the last colomn of table III.

In table V are shown some physical data for the catalysts used during the tests described in table I and II. In this table we will especially emphasize the difference in mechanical strength for the products D and F. This strength is high for both types of catalysts before the test. After 500 hours of operation the reactors were opened and the catalysts were examined.

For product F a loss in weight of 20 % was found, while the loss of weight for product D was about 2 %. A difference axially along the reactors was also observed. It is assumed, regardless of the validity of the patent,

that the reason for this large difference of the mechanical stability of the catalyst is that the binding forces in the pellets are related to the content of zinc oxide in product F while this is not the case for product D. Formation of a liquid zinc chloride phase for product F will result in substantial weakening of these forces. This explains the large difference in mechanical strength axially in the reactor filled with catalyst F. There is not observed any difference between catalysts of type A and D without zinc oxide and of the type C and D with zinc oxide regaring mechanical properties. The zinc oxide present in catalyst C will not take part in binding together the pellet because it was added to the already formed pellet. Even if a liquid zinc oxide phase should be formed in this product, it would therefore not lead to a substantially weaking of the pellet.

The results in table IV show that it is significant how the zinc oxide is added to the catalyst.

As shown in table III, the catalysts A-E have higher initial activity than the known catalyst F. When technical reaction gas (table II) is used, the catalyst C according to the invention maintain its high activity while catalyst F gets a significant drop in activity after a short period of operation, and then it stays at a fairly constant level. When reaction gas having a relatively high content of chlorine is used (table III), the known catalyst F gets approximately the same drop in activity as in technical gas. Contrary to this the catalysts C and E, according to the invention, maintain their high activity even when chlorine is present in the reaction gas. The activity of catalysts A and D, which contain no zinc oxide, get a significant drop in activity in gas containing chlorine. Accordingly

catalysts C and E have a higher activity than the known catalyst F and are at least as resistant as that one regarding chlorine poisoning.

The advantage of using alkali carbonate (Example 1b and 4b) is primarily related to the filtrate which thereby contains less heavy metals, expecially copper. From an evironmental point of view the filtrate will therefore be somewhat easier to take care of than in the case when ammonium carbonate is used. When ammonium carbonate is used, it will also be an advantage that the catalyst production is close to a fertilizer plant which can make use of the NH_4NO_3-containing filtrate.

Which precipitating agent should be used, will first of all depend on lokal conitions for using the by-products.

Further, the catalysts according to the invention have at least as high activity as the catalysts according to US-patent No. 3,787,382. This is based on the information given in the patent. Additionally, the catalysts of type C and E are substantially more resistant to chlorine poising than the known catalyst.

The most essential features of the catalyst according to the invention are that it comprises a copper oxide, aluminium oxide -spinel, that 60-100 % of the copper present is bound to aluminium oxide as copper oxide, aluminium oxide -spinel and that the zinc oxide of the catalyst exists in the pores of the spinel.

Even if it is advantageous that as much as possible of the copper is bound in the copper oxide, aluminium oxide -spinel, it has been found that also when only 60 % of the copper is bound in this way, it is obtained

an excellent catalyst. The atomic ratio Cu:Al is not very critical as long as it is whithin the range 0.25-0.50. Regarding the content of zinc oxide in the catalyst, it has been found that even as little as 1 weight per cent zinc oxide in the pores of the spinel gives a positive effect. How much zinc oxide there should be in the pores of the spinel depends on practical conditions and the content of contaminants in the gas in which the catalyst shall be used. It has been found that up to 20 weight per cent zinc oxide in the pores of the spinel can be advantageous in certain cases.

The most essential feature of the method is the precipitation of the copper- and aluminium salts at pH 6.0-6.5, the calcination step for obtaining a good spinel structure and finally the incorporation of zinc oxide in the pores of the spinel.

As shown in the above examples and table IV, it is not only the catalyst's content of copper and zinc which are decisive to this activity and life time. It is also critical in which form the components are present in the catalysts.

Also regarding mechanical properties, it has been found (table V) that the catalysts C and E according to the invention, are better than the known catalyst F. Such a great loss of catalyst mass as observed during the test can ledad to increasing pressure drop in a technical reactor, and it can also lead to channeling of the gas trough the catalyst layer (bed). This means that it may be necessary to replace the catalyst after a relatively short period of operation, even through the catalyst as such has an acceptable high activity. For the catalyst C and E, which have substantially better mechanical properties, replacement for this reason will not be necesssary.

Claims

1. Catalyst comprising aluminium oxide and copper oxide where at least 60 per cent by weight of this oxide mixture consists of a copper oxide, aluminium oxide compound having a spinel structure, characterized by that 60-100 % of the copper present is bound to aluminium oxide as copper oxide, aluminium oxide -spinel and that the atomic ratio Cu:Al = 0.25-0.50 in the spinel structure, and that as known per ce, the catalyst contains zinc oxide and that the zinc oxide is present in the pores of the spinel in an amount of 1-20 per cent by weight calculated as zinc oxide, and that the catalyst possibly contains further amounts of zinc oxide which is admixed mechanically or is present as a coatingon the catalyst.

2. Catalyst according to claim 1, characterized by that 90-100 % of the copper present is bound as copper oxide, aluminium oxide -spinel and that the catalyst contains 2-12 per cent by weight of zinc oxide in the pores of the spinel.

3. Method for preparing catalysts according to claim 1 and 2, comprising precipitation of metal salts, filtering, drying, calcing and tableting, characterized by that a solution of copper- and aluminium nitrate is mixed with a solution of ammonium or alkali carbonate during adjustment of the pH to 6.0-6.5 for this mixture, and that the suspension thereby formed containing copper hydroxide and/or copper hydroxycarbonate and aluminium hydroxide is filtered, washed and dried, and that the dried product is calcined at 750-850° C until it is

obtained 60-100 % spinel structure, and that a zinc salt then is added to the spinel either from a aquous zinc salt solution or a zinc salt melt, whereupon the spinel thus impregnated is heated to at least the decomposition temperature for the zinc salt, whereby this salt is converted to zinc oxide, and that it possibly is added further amounts of zinc oxide which is admixed mechanically.

4. Method according to claim 3, characterized by that the spinel is impregnated by a zinc salt by means of an aqueous solution containg ZnO and NH_4HCO_3, whereupon the thus impregnated spinel is warmed until a temperature of at least the decomposition temperature of the zinc salt which is converted to zinc oxide.

5. Method according to claim 3, characterized by that the spinel is impregnated by $Zn(NO_3)_2$-solution, that solution in surplus is removed and that the impregnated spinel then is dipped in an ammonium carbonate solution for complete or partial precipitation of zinc hydroxycarbonate, whereupon the spinel thus impregnated is washed and warmed until a temperature of at least decomposing temperature for the zinc salt for formation of zinc oxide.

6. Method according to claim 3 or 4, characterized by that the tabletting is carried out after the zinc salt is converted to zinc oxide.

European Patent Office

0042471

EUROPEAN SEARCH REPORT

Application number
EP 81 10 2072

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	US - A - 3 923 694 (D.CORNTHWAITE) * Column 1, lines 7-11; column 1, line 65 - column 3, line 56; claims 1,5-9 *	1-3,5, 6	B 01 J 23/00 23/80 C 01 B 3/12
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	DE - A - 2 302 658 (IMPERIAL CHEM. IND) * Page 2, paragraph 3 - page 7, paragraph 2; claims 1-3,6-9 *	1-3,6	
	--		TECHNICAL FIELDS SEARCHED (Int. Cl.3)
	DE - A - 1 542 222 (IMPERIAL CHEM. IND) * Page 1, paragraph 1; page 2, paragraph 3 - page 6, paragraph 1; example 1; claims 1,3-6 *	1-3,5, 6	B 01 J 23/00 23/80 23/72 C 01 B 3/12
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	DE - A - 1 542 044 (CATALYSTS AND CHEM. IND.) * Page 2, paragraph 2; page 7, paragraph 2 - page 10, paragraph 1; claims 1,2,6,7 *	1,3,6	
	--		CATEGORY OF CITED DOCUMENTS
A	DE - A - 1 905 547 (CHEMETRON CORP.)	4,5	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
A	FR - A - 2 418 025 (CHEVRON RES. COMP.)		
A	DE - A - 2 652 556 (TOYOTA JIDOSHA KOGYO K.K.)		
	----		&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10-08-1981	PFANNERER